

Energy levels and radiative rates for Cr-like Cu VI and Zn VII

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Abstract

Energy levels and radiative rates (A -values) for transitions in Cr-like Cu VI and Zn VII are reported. These data are determined in the quasi-relativistic approach (QR), by employing a very large *configuration interaction* (CI) expansion which is highly important for these ions. No radiative rates are available in the literature to compare with our results, but our calculated energies are in close agreement with those compiled by NIST and other available theoretical data, for a majority of the levels. The A -values (and resultant lifetimes) are listed for all significantly contributing E1, E2 and M1 radiative transitions among the energetically lowest 322 levels of each ion.

Received 11 February 2016; Accepted 11 Month 2016

Keywords: Cr-like ions, energy levels, radiative rates, oscillator strengths, line strengths, lifetimes

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1. Introduction

Recently, we reported energy levels and radiative rates (A -values) for transitions in Cr-like Co IV and Ni V [1], and here we provide similar results for two other ions, namely Cu VI and Zn VII. Generally, ions with $Z \leq 30$ are important for the study of astrophysical plasmas. However, they may also be relevant to research in fusion plasmas, because often some of them are constituent of the reactor walls as impurities. There are several observed lines of both Cu and Zn ions (see for example the CHIANTI database [2, 3] at <http://www.chiantidatabase.org>), but we are not aware specifically of those for Cu VI and Zn VII. However, many of their lines in the 157–243 Å wavelength range are listed in the *Atomic Line List* (v2.04) of Peter van Hoof (<http://www.pa.uky.edu/~peter/atomic/>), because these are useful in the generation of synthetic spectra. Inspecting the atomic and molecular database Stout [4], one can see that there are only incomplete sets of level energies for both Cu VI and Zn VII, whereas radiative transition data are completely absent. Additionally, ions of Cu have been identified of particular interest to fusion studies [5], and hence their atomic data are required for the modelling of such plasmas.

Poppe et al. [6] were the first to measure energies for levels of the $3d^6\ ^5D$ and $3d^5(^6S)4p\ ^5P^o$ configurations of Cu VI from a laboratory spectrograph. Soon after, van Kleef et al. [7] extended their work to measure additional lines of the $3d^5(^4P)4p\ ^5P^o$ and $3d^5(^4D)4p\ ^5D^o$ multiplets, classifying 29 levels in total. Based on these identifications, van het Hof et al. [8] calculated energies for the levels of the $3d^6\ ^5D$ term. They used *least square fitting* of Slater-Condon parameters, and their calculations were biased towards the known (observed or measured) results and iso-ionic, iso-electronic and iso-nuclear trends. As a result, their theoretical energies differed between -4.6% and $+3.3\%$ with the measurements. However, they also predicted an energy for one additional level, i.e. $3d^5(^4S)4p\ ^3P^o_0$. The work of [8] was further extended by Uylings and Raassen [9] who predicted energies for an additional 6 levels of the $3d^54p$ configuration. However, the most extensive experimental and theoretical work has been performed by Raassen and van Kleef [10] who identified most of the levels of the $3d^6$, $3d^54s$ and $3d^54p$ configurations of Cu VI. Their listed (and other) energies have been compiled and assessed by Sugar and Musgrove [11], and their recommended values are also available on the NIST (National Institute of Standards and Technology) website [12]. However, there are a few gaps in the energy spectrum (including the 1S_0 level of the ground configuration $3d^6$) – see Section 2 and Table ?? . Furthermore, no A -values are available in the literature for transitions of Cu VI, and therefore the aim of the present paper is to complete the spectrum by predicting energies for the missing levels, as well as to calculate the A -values.

To date the most complete experimental investigation for the energy levels of Zn VII has been performed by van het Hof et al.

[13], whose results have been compiled, assessed and recommended by Sugar and Musgrove [14], and are also available at the NIST website [12]. However, many levels (in fact more than for Cu VI) are missing from this compilation (see Section 2 and Table ??), and therefore we have performed our calculations to predict energies for the missing levels as well as to report the A -values, which are not available in the literature.

2. Energy levels

In this work, as in our other recent studies, we have employed the quasi-relativistic approximation (QR), described in detail elsewhere [15], to determine level energies, radiative lifetimes (τ) and various transition parameters among the levels of the ground configuration $3d^6$ and two lowest excited configurations $3d^54s$ and $3d^54p$ in Cu VI and Zn VII. The calculations performed here are similar to those for Co IV and Ni V [1], and as for those ions, we have also made test calculations with the general-purpose relativistic atomic structure package (GRASP) and the flexible atomic code (FAC). However, energies obtained with both these codes show just as large discrepancies with measurements, in magnitude and orderings, as shown in table A of [1] for Co IV. Therefore, we discuss our theoretical results generated only in the QR approximation.

The one-electron radial orbitals (RO) for the electrons of the investigated configurations $3d^6$, $3d^54s$ and $3d^54p$, and for the $4d$ and $4f$ electrons, were determined from the quasi-relativistic Hartree-Fock equations described in [16, 17]. In the QR calculations, relativistic effects are included through the Breit-Pauli approximation adopted for the quasirelativistic approximation [15]. To include the correlation, all one- and two-electron promotions from the 3ℓ and 4ℓ electron shells of the investigated configurations are considered in a large CI wavefunction expansion. For electrons with $5 \geq n \geq 8$ and $\ell < n$, which describe virtual excitations, the transformed radial orbitals (TRO) are employed [15]. The admixed configurations generated in this way produce over 10^9 configuration state functions (CSFs), which makes the further calculations of A -values intractable. Therefore, we select only those admixed configurations that have the largest contributions to the CI wavefunction (see, e.g. [18]). Following these procedures, the resultant CI basis consists of 425 even and 256 odd configurations of Cu VI, producing 669 075 and 991 598 CSFs, respectively. In the case of Zn VII, we include 398 even and 241 odd configurations generating 648 845 and 960 686 CSFs, respectively. As one can see from these numbers, the admixed configurations produce a very large set of CSFs even after the reduction procedures, described in [19]. Because of this, we must limit the number of the admixed configurations by increasing the selection criterion to 10^{-5} , and consequently some important configurations are omitted. Therefore, we cannot produce a satisfactory agreement of our results with the available measured energy levels for Cu VI and Zn VII. To improve the accuracy of the calculated data, all Slater integrals describing the LS -dependent interactions are (slightly) reduced by 2.5% for Cu VI and by 2.3% for Zn VII.

The energies obtained in the QR approximation are listed in Table ?? for all 322 levels of the $3d^6$, $3d^54s$ and $3d^54p$ configurations of Cu VI, along with the NIST values. Among the lowest 34 levels of the $3d^6$ ground configuration, the maximum discrepancy between theoretical and experimental energies (for any level) is much less than 1%, except for the levels of the lowest term 5D where it is above 1% and reaches a maximum of 1.6% for the level 2 (5D_3) – but even in this case the absolute energy deviation is just 19 cm^{-1} . This is caused by insufficient accuracy in the calculation of the spin-orbit interaction. The accuracy achieved here is better than that achieved for Co IV and Ni V [1], because of the improvements made in our calculations. Furthermore, the discrepancies between the theoretical and experimental energies are much lesser – usually less than 0.2% and not worse than 0.3% – for the remaining levels belonging to the excited configurations $3d^54s$ and $3d^54p$. We note that energies for many levels are missing from the NIST compilation (or the literature) and therefore, we have predicted energies for such levels – see e.g., 62–89 in Table ?. Since the maximum discrepancy with the measurements among the levels of the excited configurations is less than 0.3%,

it should be a robust measure of accuracy for our predicted energies. Finally, the energy orderings between theory and measurement are nearly the same, although there are a few minor differences for close-lying levels, such as 28–29 and 38–42.

However, the *LSJ* designations listed in the table are not always definitive, because we have performed just a formal identification based on the maximum percentage contribution of CSF in the CI wavefunction expansion, and some levels are highly affected by CSFs mixing. For this reason their description using just a *LSJ* notation is not definitive in all cases, and other level identification scheme have to be applied instead of an *LS* designation. All such levels are shown by a superscript “a” or “b” – see e.g., levels 214, 220 and 269. However, we stress that this problem is not unique to our code or our QR approximation. It is a general atomic structure issue and applies to all such large calculations, by any code. This is why a large number of the $3d^54p$ levels have no identified *LS* terms in the NIST database [12].

In Table A we compare our calculated energies with the theoretical work of Raaasen and van Kleef [10] and Uylings and Raassen [9] for common levels, but only for those for which experimental results are not available – see their tables III and IV. For all these levels there are no appreciable discrepancies among the three independent calculations.

Our calculated energies for the levels of Zn VII are listed in Table ?? along with those of the NIST compilation, which are available for about 50% of the levels but cover almost the entire energy range. As for the Cu VI results in Table ??, the discrepancies with our calculations are smaller than 1% for the lowest 34 levels of the $3d^6$ ground configuration, except for levels 2–5, for the same reason as for the ground configuration levels of Cu VI. However, the agreement with measurement is significantly better – usually better than 0.05% and no worse than 0.1% (in only a few cases) for the levels of the excited $3d^54s$ and $3d^54p$ configurations. This should be indicative of the accuracy of our predicted levels, missing from the NIST compilation. Since data for the $3d^54s$ level energies in the NIST compilation are missing, we assume our calculated results can serve as benchmarks for these levels.

3. Radiative rates

To our knowledge, *A*-values are not available in the literature for radiative transitions in Cu VI and Zn VII. Therefore, in Table ?? we list transition energies (ΔE , cm^{-1}), wavelengths (λ , Å), emission radiative rates (*A*-values, s^{-1}), weighted oscillator strengths (*gf*, dimensionless), and transition line strengths (*S*-values in atomic units) for the E1 (electric dipole), E2 (electric quadrupole), and M1 (magnetic dipole) transitions of Cu VI among all 322 levels summarised in Table ?? belonging to the lowest 3 configurations $3d^6$, $3d^54s$ and $3d^54p$. Similar results for Zn VII are presented in Table ?. Only those *A*-values are listed in Tables ?? and ?? which are $\geq 10\%$ of the largest value for an emission transition probability *A* from the upper level *j*. This means that very weak transitions are not included to save on space, as their impact on the modelling of plasmas shall be negligible. Due to this selection, the *A*-values for magnetic quadrupole (M2) and electric octupole (E3) transitions are not included in Tables ?? and ??, although their data are calculated. However, all the level energies and the radiative transition parameters, such as transition wavelengths, transition probabilities, oscillator strengths and line strengths for the E1, E2 and M1 transitions determined in the QR approximation, along with electron-impact excitation data determined in the plane-wave Born approximation, are freely available in the ADAMANT database at Vilnius University (<http://www.adamant.tfai.vu.lt/database>). We note that the E3 and M2 transitions are very weak (i.e. smaller than 1% of the strongest transition), and therefore their transition parameters have no entries in this database.

Since no other data for *A*-values are available in the literature, it is difficult to assess the accuracy of our calculations. However, since our calculated energies are reliable to better than 1% for a majority of levels, the corresponding data for *A*-values are likely to be reasonably accurate. Based on conclusions given in [1] and the assessment of the radiative transition data determined in the QR

approximation from our previous work, we are confident that the current A -values are reliable and can be adopted in plasma spectra modelling.

To allow the application of our data to the modelling of absorption spectra, in Tables ?? and ?? we list λ and f -values for all *comparatively strong* absorption E1 transitions, i.e. those having $f \geq 0.10$. We note that not all important absorption transitions are present in Tables ?? and ?. These transitions do not normally vary much with differing CI expansion basis. However, the remaining weak(er) transitions may show large variations with other independent calculations, as they are more susceptible to changes arising from differing sizes of the CI wavefunction extension and varying the calculation method. Also in Tables ?? and ?? we present λ and f -values for some weaker absorption lines originating from the lowest 5 levels of the ground configuration term $3d^6\ ^5D$. These lines may be useful for modelling the absorption spectra of low-temperature plasmas, as all the lowest levels of the 5D term are close.

4. Radiative lifetimes and Landé g -factors

The radiative lifetime τ of a level j is determined as $1.0/\sum_i A_{ji}$, where the sum is over all calculated radiative decay channels with $i < j$. As for the A -values, no prior theoretical or experimental results are available for τ for the two ions discussed here. Therefore, the accuracy of our calculated τ should be no worse than that for the A -values. Mainly it depends on the strongest emission transitions for a particular level, as the influence of (numerically more) weak(er) transitions in the above sum is less important. For the convenience of future workers, in Tables ?? and ?? we summarise our values of τ for all levels.

Also listed in the tables are the Landé g -factors, which show how the energy levels split in a magnetic field. These are dimensionless coefficients describing the Zeeman effect for a particular LSJ level. In the case of a multi-term, multi-configuration wavefunction, the Landé g -factor is expressed as:

$$g = 1 + \sum_{CLS} \alpha(CLSJ)^2 \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \quad (1)$$

Here g is the Landé g -factor, the sum is over all CSFs for that level, C represents the configuration, LSJ are total moments of the level, and $\alpha(CLSJ)$ is the percentage contribution of a particular CSF for the level eigenfunction. Comparing the theoretical values of g with experiment, one can assess the quality of a multi-reference wavefunction.

5. Conclusions

Energy levels and radiative rates for transitions in Cu VI and Zn VII have been determined in the QR approximation. For the calculations, a very large CI wavefunction expansion basis has been adopted which helped to reduce the discrepancies between theory and measurement for energy levels. For the Cu VI ion, based on comparisons with measured (and limited theoretical) results, our energy levels of the excited configurations are assessed to be accurate to better than 0.2% for most levels. In the case of the ground configuration levels, the accuracy usually is no worse than 0.7%, only with data for the lowest 5 levels (term 5D) being somewhat less reliable, but their absolute energy discrepancies do not exceed a few tens of cm^{-1} . For the Zn VII ion, these differences are even smaller, and do not exceed 0.5% for the excited configuration levels. The accuracy of the ground configuration level energies is approximately the same as for Cu VI.

Our calculated energies are listed for all 322 levels originating from the $3d^6$, $3d^54s$ and $3d^54p$ configurations, cover a much larger range than other available theoretical or experimental results, and is a complete set of energy levels for these three configurations.

This is important as there are no available data for the $3d^54s$ configuration of Zn VII, whereas only a few level energies have been determined for Cu VI to date.

Corresponding data for radiative transition rates have also been calculated and listed for the E1, E2 and M1 emission transitions among these 322 levels. However, due to the paucity of prior results no comparisons (and hence accuracy assessments) can be made. Nevertheless, the accuracy achieved in the determination of energy levels, as well as the good agreement of A -values for similar multi-electron systems demonstrated in our previous publications, indicate our A -values should be reliable, particularly for comparatively strong transitions.

A significantly extended data set for the Cu VI and Zn VII energy levels, including not only their identification but also the wavefunction percentage composition, are freely available from our database ADAMANT. In this we present much more extensive results on the radiative transition parameters, including weaker transitions with a selection criterium decreased by a factor of 10. Electron-impact excitation cross sections and rates are also tabulated in ADAMANT. We believe our present data will be useful for the modelling of plasmas as well as for further accuracy assessments.

Acknowledgments

The work at QUB has been partially funded by AWE Aldermaston.

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Table A

Comparison of energies (in cm^{-1}) for some levels of Cu VI – see Table ?? for all levels.

Index	Configuration	Level	RK81	UR96	Present
34	$3d^6$	1S_0	150319		149833
115	$3d^5(^4P)4p$	$^3D_1^o$	391590	391991	392553
116	$3d^5(^3P)4p$	$^5D_0^o$	392085	392060	392583
265	$3d^5(^5S)4p$	$^3P_0^o$	438365	438485	438912
304	$3d^5(^3P)4p$	$^1S_0^o$	487714	487136	486762
315	$3d^5(^3D)4p$	$^3D_2^o$	505688	505800	505334
322	$3d^5(^1D)4p$	$^1P_1^o$	517278	517241	517447

RK81: Raassen and van Kleef [10]

UR96: Uylings and Raassen [9]